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ABC of kink kinetics and density in a complex solution.

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Abstract. This tutorial lecture explains the ways supersaturation in complex solutions may be introduced to be most relevant to describe experimental data on kink and step kinetics. To do so, we express the kink rate via the frequencies of attachment and detachment of the building units and then link these frequencies to the measurable activities of these units in solution.

Possible reasons for violation of the Gibbs-Thomson law are briefly discussed with reference to our earlier work.

1. INCENTIVES TO STUDY SOLUTION GROWTH

Basic knowledge and problems accumulated by the middle of the 20-th century in crystal growth physics were summarized and resolved in the now classical theory of W.Burton, N.Cabrera and F.C.Frank (BCF) in 1951[1]. Developing the J.Frenkel's pioneering idea [2], Burton and Cabrera introduced basic concept on surface roughening. This concept allowed to understand why crystals growing from solution and vapor are mainly faceted while the crystal growing from melt acquire spherical shape. The BCF theory brought contemporary physics to crystal growth. In particular, quantitative understanding of the layer-by-layer growth of faces, steps and kinks was achieved and the Frank's idea on crucial role of screw dislocations in step generation was elaborated.

Being experimentally simple, solution growth was historically the first area in the basic academic studies of crystal growth physics and chemistry (see refs [3-5] for history), along with the much older geometrical approach of mineralogists and crystallographers. The new practical incentives for deeper insight into growth from solutions came during the World War II when growing quartz was initiated for radio frequency stabilization and classical optics and later, in the 50-s, when non-linear optics demanded KDP and other materials, like Rochelle salt - for laser frequency doubling and tripling, infrared detection, imaging etc. In the 70-80-s, the laser nuclear fusion programs in the USA, USSR, Japan and France raised even more challenging issues of extremely perfect meter-scale KDP and DKDP crystals capable not to crack, even locally, under the gigawatt scale laser pulses. In response, the fast crystal growth technology was born [6-8] allowing to reach growth rate of ~ 1 cm/day rather than traditional < 1 mm/day, keeping the crystal perfection high. Subtle defects allowing laser beam to damage these crystals below the theoretical threshold still remain a big challenge.

Since the 70-s, massive effort to decipher atomic structure of tens of thousands of biological macromolecules is on the way. This gave a big push to biomacromolecular

crystallization, also exclusively from solutions. The studies are funded by space agencies worldwide - because ~20% of crystals grown in convection free environment showed higher lattice perfection. The latter is a must to determine atomic structure of biomacromolecules which makes crystallization the bottleneck for the whole enterprise. Nevertheless, despite of humongous dissemination, deeper current insight, automation and other new know-how in practical terms, this area remains essentially empirical. One of the reasons is extreme chemical complexity and variability of surfaces of the ~2- 100 nm size biomacromolecules and of solutions from which these biocrystals grow [9,10].

Biomineralization, which is also the growth from the about room temperature solutions, is aimed at several strategic puzzles to be solved. Among these puzzles are, for example, the ways Nature build bones, teeth, kidney and gallstones and how to repair the former and get rid of the latter. Mollusk shells and sea urchins are examples of interaction between the living and inorganic molecules with the perspective to understand origin of life and carbon cycle on our planet with its ecological and geological problems. Essential effort to understand growth of calcite, hydroxyapatite, brushite, oxalates and other biominerals is being successfully undertaken. Nevertheless, there are still more questions than answers in this vast area [11-13].

Preparation and handling of nanoparticles for optics and electronics, grown often from solutions in the 300-700°C range, is overwhelmingly empirical despite of its big potential practical impact [14]. Creation of the nanoparticles in complex solutions rise also of the Ostwald ripening problem since thin protection film covering each particle is still permeable for ions and so are the matrices into which the nanoparticles are embedded.

Chemical industry produces, mainly from solutions, drugs, fertilizers, paint, table salt, sugar powders subject to ageing via Ostwald and non-Ostwald ripening (the latter - via temperature variations). Understanding of the ageing also remains mainly empirical.

Chemical complexity is the common feature in both the old and more recent areas while the existing theories deal overwhelmingly with the simplest Kossel model. Computational prediction of the crystal habit based on the classical periodic bond chain approach with its assumptions on the bond strength is probably the only exception[15]. However, this approach hardly allows to understand growth kinetics.

Even relatively simple ionic solution often includes complexes of the species of which the crystal is built. Composition of these building units and their kinetic properties are usually only guessed. We do not have the rules how to identify building units and their behavior. In any crystallization driven by chemical reactions (because the desired product is slightly soluble), influence of solution composition, including stoichiometry, acidity, and temperature on the growth rate and crystal composition and perfection are the closely related important questions requiring deeper insight.

There is also another group of problems related to the slightly soluble salts, biominerals in the first place. For these materials, the surface free energy is several times higher than that for the well soluble crystals. This is indirect evidence of the high kink energy and thus of the low kink density. The latter means extremely straight, rather than rounded

steps and questions applicability of the Gibbs-Thomson law and fluctuation dissipative theorem, the cornerstones of the BCF theory.

In these tutorial notes, we will address briefly basic concepts used in treatment of crystal growth from chemically complex solutions.

2. SUPERSATURATION

2.1. Molecular solutions.

As the reference point, let us recollect the simplest case of a solution consisting of a solvent and one type of solute species (molecules) with the activity a . If a_e is the solute activity at the solution-crystal equilibrium, the absolute supersaturation may be defined as

$$\Delta a = a - a_e. \quad (1)$$

The relative supersaturation is defined either as a/a_e , or as

$$S = (a/a_e) - 1 = \Delta a/a_e. \quad (2)$$

The most general driving force for any phase transition is the difference, $\mu_L - \mu_S$, between chemical potentials, μ , of molecules in liquid L and in solid, S. This difference in kT units may be called logarithmic supersaturation

$$\sigma = (\mu_L - \mu_S)/kT \equiv \Delta\mu/kT = \ln(a/a_e). \quad (3)$$

To obtain the last relationship in eq.(3), we use the chemical potentials of a molecule in the solution and in the crystal in the form:

$$\mu_L = kT \ln \omega a + \psi, \quad \mu_S = kT \ln \omega a_e + \psi, \quad (4)$$

where ψ is the energy of interaction between the solute molecule with the surrounding species in solution. The energy ψ depends only on pressure and temperature but not on the concentration. At equilibrium, $\mu_S = \mu_L$. Unlike in conventional definition of chemical thermodynamics, the activity in eq.(4) is multiplied by molecular volume ω in the solid phase to make the quantity under logarithm dimensionless. The quantity ωa may be understood as the volume fraction of the molecules in solution times the activity coefficient. The supersaturations S and Δa are related to σ as

$$S = \exp \sigma - 1 = a/a_e - 1 = \Delta a/a_e \quad (5)$$

2.2. Solution of dissociating molecules.

Here we consider molecules dissociating in a solvent to the ions or not charged species, A and B. Then the logarithmic supersaturation

$$\sigma_{A,B} = \Delta\mu/kT = \ln a_A a_B / K, \quad \Delta\mu = \mu_{LAB} - \mu_{SAB} = kT \ln a_A + \psi_A + kT \ln a_B + \psi_B - \mu_{SAB},$$

$$K \equiv K(T,P) = \exp [(\mu_{SAB} - \psi_A - \psi_B) / kT] = (a_A \cdot a_B)_{\text{equilibrium}}. \quad (6)$$

Here the experimentally measured solubility product K is expressed via the difference between the usually unknown chemical potential $\mu_{S,AB}$ of the molecule AB in the solid and the energies ψ_A, ψ_B of the species in solution. This difference determines the energy required to replace the AB molecule from a kink on the crystal surface to solution and to dissociate it. Entropy (mainly vibrational) is present in the μ_S but is not major in the ψ_A, ψ_B . Therefore the dissolution enthalpy may be an approximate measure of this difference. The species activities in solution at equilibrium, a_{Ae} and a_{Be} , and thus the K value are measured experimentally.

Often the molecules dissociate only partly, so that molecules are also present in solution. Then we deal with three species, A, B , and AB . At equilibrium, balance between all these three species in solution and the molecules in the crystal, must be maintained:

$$\begin{aligned} \mu_{LA} + \mu_{LB} &= \mu_{SAB} \\ \mu_{LAB} &= \mu_{SAB} \\ \mu_{LA} + \mu_{LB} &= \mu_{LAB}. \end{aligned} \quad (7)$$

The first two equations present the liquid-solid while the third one presents the dissociation equilibrium within solution. Eqs. (7) mean that the log supersaturation with respect to molecules, σ_{AB} , no matter how high or low their concentration, is the same as the supersaturation with respect to the ions, $\sigma_{A,B}$:

$$\sigma_{AB} = \Delta\mu_{AB}/kT = \ln a_{AB}/K_{AB} = \ln (a_{AB}/a_A a_B)(K/K_{AB}) = \Delta\mu_{A,B}/kT = \sigma_{A,B}, \quad K_{AB} = \exp[(\mu_{SAB} - \psi_{AB})/kT]. \quad (8)$$

Therefore, adding the molecule AB as a new species for consideration, on top of the A and B , means replacing $\Delta\mu_{A,B}$ by the sum $\Delta\mu_{A,B} + \Delta\mu_{AB}$ which is equivalent to just squaring the $\sigma_{A,B}$. Thus, adding any species into which the crystal molecule, or unit cell, or any other group of molecules in the crystal may dissociate, means just taking power of the supersaturation relative to any of these species. Therefore the log supersaturation are usually divided by the number of species to which the given solid dissociates [12]. For the two ions this normalized supersaturation is:

$$\sigma_{A,B} = \ln (a_A a_B / K)^{1/2} = (1/2) \ln (a_A a_B / K). \quad (9)$$

The supersaturation, generalizing S and $\Delta a/a_e$ is then, similar to eq.(5)

$$S = \exp \sigma = (\Pi/K)^{1/2} - 1 = (\Pi^{1/2} - K^{1/2})/K^{1/2}. \quad (9')$$

For a molecule or a growth unit if n species:

$$\sigma = \Delta\mu/nkT = (1/n) \ln \Pi_i^n a_i / K_n, \quad K_n = \exp[(\mu_{SA1A2...An} - \psi_1 \psi_2 \dots \psi_n)/kT],$$

$$S = \exp \sigma = (\Pi/K)^{1/n} - 1 = (\Pi^{1/n} - K^{1/n})/K^{1/n}. \quad (10)$$

where Π denotes the product of activities from 1 to n and K is solubility product. The product $SK^{1/n}$ is analogous to Δa .

In laboratory practice, studying crystal growth kinetics, people often simply dissolve a dissociating salt in water, determine the equilibrium solubility, i.e. a_e , and then use molecular relationships eqs.(1),(2),(3) for the driving force. That works well because $a_A = a_B =$ squared equilibrium concentration so that eq.(9) is reduced to eq.(3) – ionic solution may be treated as a molecular solution. However, composition and stoichiometry of solution may be violated by changing pH or adding excess of one of the ions. In that case, the pseudomolecular approach is not valid any more and the supersaturation $\sigma_{A,B}$ averaged over the A and B should be used. Similarly, in more complex systems, the driving force eq.(10) that presents the average supersaturation per one ion should be used. The averaging, i.e. dividing $\Delta\mu$ by n , eq.(10) makes sense because, as it was mentioned above, supersaturation with respect to each of the ions involved is the same. In addition, averaging is practically more convenient since it keeps the numbers expressing activity and solubility products within the reasonable range. For instance, taking for the whole two hydroxyapatite formula units as they are present in the lattice unit cell as $\text{Ca}_{10}(\text{HPO}_4)_6(\text{OH})_2$ and taking as A,B,... the ions Ca^{2+} , HPO_4^{2-} , and OH^- ions and calculating their solubility product with their concentrations in the corresponding powers 10,6, and 2 (18 species in total) one comes to $K_{18} = 10^{117.3}$ (mol/L)¹⁸[12]. Averaging results in more convenient $K = 10^{6.5}$ mol/L keeping the same sense. It is, however it is a matter of kinetics how to determine kinetic coefficient, if any, to properly describe crystal face, step or kink rate or rate of nucleation with these different forms of supersaturation.

The chemical potential difference, $\Delta\mu$, i.e. the log supersaturation, enters the nucleation work along with the volume ω of the growth unit this $\Delta\mu$ is related to as the ratio $\omega^3/\Delta\mu^2$ for the 3D nucleation or as $\omega^2/\Delta\mu$ for the 2D nucleation. Because of these different exponents at the volume and at the $\Delta\mu$, normalization of $\Delta\mu$ to the number of neither ions, nor molecules, nor molecules per lattice unit cell leaves the nucleation work invariant. In other words, the nucleation work depends on our choice of the growth unit making the calculation about useless unless we know what these units are. This is the problem of the growth units. This problem exists also for the kink and step propagation rate. It is generating many uncertainties in both the nucleation and growth analyses. Therefore understanding of what definition of supersaturation is the most relevant for any specific case is important. Vice versa, carefully measuring the relevant propagation rates, one may hope to get information on the growth units. In what follows we will consider the kink kinetics.

3. KINK KINETICS.

3.1. Kink position. The upper image in Fig 1 shows schematically kink position at the step in the simplest case of the so called Kossel crystal model. This is just a simple cubic lattice (or its topological equivalent, like FCC or diamond lattice). Thus each molecule in

the bulk has six neighbors while the one in the kink position has three neighbors. In a Kossel crystal, there are only one type of kinks, no matter what the crystal face is. In the non-Kossel crystal, there are several types of kinks terminated by either different species e.g., ions, or by exactly the same molecules occupying not equivalent position in the lattice unit cell, as shown in the lower drawing in the Fig.1, or both. Different kink configurations possess different energies.

Kossel Crystal

Non-Kossel crystal

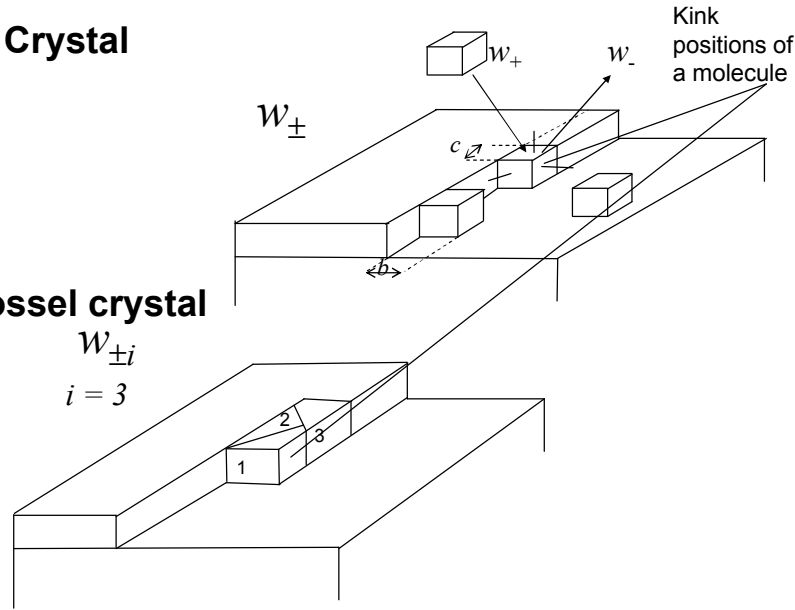


Figure.1. There is only one type of kinks at the step on the Kossel crystal and several types on the non-Kossel crystal (see the text above). A scheme allowing three possible non-Kossel kinks is shown. The frequency of attachment and detachment are w_+ and w_- , respectively.

On the Kossel crystal surface, detachment of a molecule from the kink does not change interfacial energy (so that chemical potential in the kink equals that of the crystal). On the non-Kossel surface, this statement is correct only for the unit cells as a whole. This property makes the kink position the gate to the crystal. That is why its behavior is so important. The kinks may be visualized by STM on conducting materials, like metals or semiconductors [16] or by AFM on proteins with their large molecules [10]. However, the temporal resolution is in the scale of a second at best. Even with proteins, this is far too long as compared with the reciprocal frequencies of attachments and detachments. The average kink density, nevertheless, may be measured directly [16,17]. What is doable, is to measure step velocity, v_{st} .

3.2. Molecular solution. For geometrical reasons, v_{st} is just the product of the kink velocity, v_k and the kink density along the steps, b/λ :

$$v_{st} = (b/\lambda)v_k, \quad (11)$$

where b is the kink depth (Fig.1) and λ is the average interkink distance. We will briefly discuss the kink density in Sec.4. The kink velocity is evidently

$$v_k = c(w_+ - w_-) \quad (12)$$

where w_{\pm} are the frequencies of attachments(+) / detachments(-) of the growth unit to/from the kink and c is the length per the growth unit in the crystal lattice along the step (Fig.1).

The Gibbs distribution of statistical mechanics says that the probability to find a particle which chemical potential is μ in a state with the energy E equals to $\exp[(\mu-E)/kT]$. We now assume that this is an activated state on top of the potential barrier E that the growth unit must overcome to join the crystal at the kink. In inorganic solutions, this barrier (10-20kcal/mol [18,19]) is associated mainly with partial dehydration of a molecule attaching to the crystal or hydration of a detaching molecule (though there is no direct experimental proof). In proteins, contribution from rotational entropy of big molecules and of water seems also to be significant. If ν is the thermal vibration frequency of the growth unit, then

$$w_+ = \nu \exp[(\mu_L - E)/kT], \quad w_- = \nu \exp[(\mu_S - E)/kT]. \quad (13)$$

The frequencies $\nu \exp(-E/kT)$ of the $L \rightarrow S$ and the $S \rightarrow L$ transitions are, on average, the same at equilibrium assuring the balance $w_+ = w_-$. In that sense, one should more rigorously think on the chemical potential rather than on the energy E of species in the activated state on the top of the barrier E . Here we ignore this difference. Less formal reason for the equality between the L to S and S to L transition barrier is that the energetically lowest reversible hydration-dehydration path is the same in both directions. When the hydration-dehydration reaction is controlled by electron transition rather than molecular vibrations or arrival of species to the kink site, the frequency $\nu \sim kT/h$ where $h = 6.63 \cdot 10^{-27}$ erg.s is the Plank constant [20]. Substituting eqs.(13) into eq.(12), one obtains:

$$v_k = \nu \exp[(\psi - E)/kT] \omega(a - a_e) \equiv \beta_k \omega(a - a_e), \quad \text{where} \quad \beta_k \equiv \nu \exp[(\psi - E)/kT]. \quad (14)$$

The eq.(14) defines the kink kinetic coefficient β_k . Evidently, from eq.(11), kinetic coefficient for the step is

$$\beta_{st} = (b/\lambda) \beta_k. \quad (15)$$

The fundamental feature of eq.(14) is the linear relationship between the supersaturation Δa , eq.(1), and the kink rate. This linearity follows from statistical independence of attachments and detachments at a kink. As we shall see below, this feature, rigorously speaking, is missing when there are more than one type of the crystal building units in solution and the sequence of species in the lattice is strictly determined, say, by strong electrostatic interactions as in all ionic systems. Eqs.(14) and (15) demonstrate also that

the absolute supersaturation Δa , eq.(1) is, unlike σ , eqs.(3) or (9), is the one at which the linearity holds. If the interkink distance, λ , is independent on supersaturation, the step velocity is also linear in Δa . This should be the case if the kinks are generated by equilibrium thermal fluctuations at the rate strongly exceeding mutual annihilation of the kinks during growth.

Last but not least, the activities a and a_e are proportional to the solution concentrations, $C(1/\text{cm}^3)$. Therefore, the eq.(14) with Δa rather than the similar with the σ , eq.(3), fits the important common sense that the growth rate is proportional to the density of crystallizing species in solution, more precisely, to ωC , the ratio of the solution to the crystal molecular number density. The reason for that scaling is that the transition frequencies, eq.(13), are proportional to the $\exp(\mu/kT)$ rather than to chemical potential itself and thus the frequency difference, eq.(12), scales as $\exp(\Delta\mu/kT)$ rather than just $\Delta\mu$.

3.3. Solution of dissociating molecules. Let us now consider the simplest NaCl type crystal built of two types of ions, A and B in solution containing only these ions. Though NaCl may be an example, ironically, for unknown reasons, nobody succeeded to grow any perfect alkali halide crystal from pure solution!. For the binary crystal, there are four independent frequencies, $w_{\pm A,B}$. Then the kink velocity [21,22]

$$v_k = 2c (w_{+A}w_{+B} - w_{-A}w_{-B}) / (w_{+A} + w_{+B} + w_{-A} + w_{-B}) \quad (16)$$

where now $2c$ means the length along the step per two species, A and B. Each of the frequencies $w_{\pm A,B}$ has the form of eq.(13). While the attachment frequencies are expressed via the known activities of species in solution, the detachment frequencies are expressed via the product $(a_A \cdot a_B)_e$ with any pair of activities at equilibrium and thus the ratio between the two may be chosen arbitrarily. Alternatively, the transition frequencies follow from the unknown chemical potential on top of the activation barrier and vibration frequencies (cf. eq.(13)). The transition frequencies, however, should depend mainly on the temperature and pressure, T and P , because the potential barrier height and vibration or electronic frequency, to the first approximation, should not depend on the solution composition. Thus the missing ratio between the detachment frequencies may be expressed via a quantity g which depends only on T, P :

$$g(T, P) = w_{-A}/w_{-B}. \quad (17)$$

Then, since $w_{-A}w_{-B} \sim K$ we have $a_{Ae} \sim (Kg)^{1/2}$ and $a_{Be} \sim (K/g)^{1/2}$. Analogously, introducing the measurable stoichiometric ratio $r = a_A/a_B$ in solution, and the product of actual activities $\Pi \equiv a_A a_B$ the activities may be expressed as $a_A = (\Pi r)^{1/2}$, $a_B = (\Pi/r)^{1/2}$. Assuming then for simplicity that all the factors $v \exp(-E/kT)$ and ψ for $+, -, A, B$ are equal to one another we obtain from eq.(16) [23]:

$$v_k = \omega v \exp[\psi_A + \psi_B - E/kT] (a_A a_B - K) / [(\Pi r)^{1/2} + (\Pi/r)^{1/2} + (Kg)^{1/2} + (K/g)^{1/2}]. \quad (18)$$

We arrive at the relationship for the kink rate of the structure similar to eq.(14). The driving force replacing $\Delta a = a - a_e$ is $\Delta \Pi \equiv \Pi - K$. This is the difference between the

products of the actual activities, Π , and the equilibrium product, K , rather than activities of the molecule. At $a_A = a_B$, eq.(18) is reduced to the eq.(14). This is the reason why treatment of growth kinetics for many ionic crystals in about stoichiometric solutions works well as if that is a molecular solution.

Similarly to eq.(1), $\Delta\Pi$ comes from the exponent $\exp(\Delta\mu/kT)$ rather than from the difference in chemical potentials $\Delta\mu = \mu_{LA} + \mu_{LB} - \mu_{SAB}$ that leads to the log supersaturation, eqs.(3), (9). However, the kink rate eq.(18) is neither proportional to $\Delta\Pi$ nor to $S = (\Pi/K)^{1/2} - 1$ because of the denominator in eq.(18), except for the cases mentioned above. Only at $S \gg 1$, we may generally expect $v_k \sim \Pi^{1/2}$, i.e. to the concentration of ions. Only at such high supersaturations, the kinetic coefficient may be taken as $\omega \exp[\psi_A + \psi_B - E/kT]$, ignoring denominator in eq.(18).

The non-linearity of v_k dependence a_A and a_B on comes from the strict ABABA... order of species in the lattice, i.e. from correlations in selection kinetics– the attachments and detachments are not completely random. Rather, attachment of A is impossible unless B is in place. In other words, there exists cooperative interaction within the unit cell AB.

It is well known, however, that the growth rate of many dissociating salts may be treated as if only molecules are present in solution, i.e following eqs.(1),(3) and (12). In particular, the step rate is often linear function of Δa . We may guess that there is strong electrostatic coupling between cations and anions in solution. Also, one may expect that activities of the cations and anions are automatically adjusted to be in stoichiometric relationship in the immediate vicinity of steps and kinks by the strict balance between the cations and anions entering the crystal. More experiments are needed to reveal the factors that force ionic solutions to mimic behavior of the molecular solutions.

The denominators in eqs.(16), (18) is responsible for dependence of the growth rate on solution stoichiometry. Evidently, at $\Delta\Pi = \text{const}$, the kink rate should reach a maximum at some ratio r . The simple reason comes again from the common sense – at low concentrations of either A or B this rate must be low and limited by the low probability of having an ion A near the kink if $r \ll 1$ or of the ion B at $r \gg 1$. Position of the $v_k(r)$ maximum on the r -axis depends on the frequency factors dropped in eq.(18). A maximum in the $v_{st}(r)$ was experimentally found in our AFM measurements of the step rates on calcium oxalate monohydrate $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ assuming that only the Ca^{2+} and $\text{C}_2\text{O}_4^{2-}$ are present in solution [23]. However, in this work the supersaturation was determined under the assumption of full dissociation and correction may change the result [24].

If the lattice is built of three different species, A,B,C, the dependence of kink velocity on the attachment and detachment frequencies is calculated to be [23]:

$$v_k = 3c (w_{+A}w_{+B}w_{+C} - w_{-A}w_{-B}w_{-C}) / (w_{+A}w_{+B} + w_{+B}w_{+C} + w_{+C}w_{+A} + w_{-A}w_{-B} + w_{-B}w_{-C} + w_{-C}w_{-A} + w_{+A}w_{-B} + w_{+B}w_{-C} + w_{+C}w_{-A}). \quad (19)$$

Here $3c$ is the length of the unit cell ABC along the step. Making again use of eq.(13) it is easy to show that the numerator is proportional to the difference between the product of the actual activities of all species A,B, and C in solution and the solubility product of these species. Denominator in eq.(19) is a sum of nine binary frequency products that is split into three groups of three products in each. In the first group, each product includes only attachments, in the second - only detachments, and in the third - one attachment and one detachment frequency. The pair of indices follow cyclic permutations of the contacts AB,BC,CA. Following the same arguments we may conclude again that there is no linear dependence of the kink rate on supersaturation in any form reviewed above, $\Delta\mu/kT$ or $\exp \Delta\mu/kT \sim \Pi - K$. However, at large supersaturations the denominator is the sum of terms proportional to $\Pi^{2/3}$, $(\Pi K)^{1/3}$ and $K^{2/3}$, so that at large Π and at $K = \text{const}$ the kink rate scales as $\Pi^{1/3}$. This suggests, again, that taking supersaturation as $\exp\sigma$ is the most relevant way for the kink and step kinetics. It is a matter of future to identify the growth units and the dependence of the kink and step rates on the driving force and stoichiometry.

4. KINKS AND GIBBS-THOMSON LAW

It is well known [1] that kink density on a step is $\sim c \cdot \exp(\varepsilon/kT)$ where ε is the additional step energy associated with creation of this kink. The kink energy may be estimated as the step energy times the length per the growth unit of which removal creates two kinks of the opposite site. Even more rough empirical estimate follows from measurements of the surface energy averaged over all crystal faces on the basis on nucleation data [25]:

$$\varepsilon/kT \approx -0.272 \ln C_e (\text{mol/m}^3) + 2.82. \quad (20)$$

A nucleus surface includes significant portion of rounded edges and corners so that their lower free energy from this contribution to eq.(20) is large. Also, nucleation in at least some of the numerous experiments summarized by eq.(20) may be heterogeneous. Therefore eq.(20) may be considered as a lower estimate. The lower is solubility, the larger is the kink energy and therefore the lower kink density. On orthorhombic lysozyme, there have been observed extremely straight steps where the average distance between kinks was measured to be $\sim 600\text{nm}$, or ~ 100 lattice spacing [17]. We may expect that the interkink distance is large as compared to the lattice spacing on all steps strictly following crystallographic orientations with simple Miller indices. Calcite and brushite are biominerals examples. When development of a spiral step around outcrop of a screw dislocation was measured, it was found that the length of the critical step segment starting with which this segment propagates normal to itself is of the order of the interkink distance [26]. It was found also that on brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) reentrant corner expedite step propagation. These finding put into question two basic assumptions of the current theory, BCF included: 1. Intensive thermal meandering of steps which is equivalent to the fast kink generation and applicability of the fluctuation dissipative theorem [20], 2. Applicability of the Gibbs-Thomson law (GTL) predicting the shift of the supersaturation above a short step segment or a small crystallite. These issues have been discussed in several publications [26, 27,28] and will not be discussed here in detail.

However, two notes, highlighting simple physics of these still not well studied phenomena should be made.

The inapplicability of the GTL comes from the fact that, unlike in liquids, the GTL in solids, is implemented only by step or surface fluctuations. If these fluctuations are slow, as with a step possessing low kink density, the GTL implementation may take time longer than allowed by other processes on a surface growing at sufficiently high supersaturation. This “high”, however seems to really low.

The supersaturation S , eq.(2) should be of the order of reciprocal length of the step segment measured in lattice spacing. If this length is ~ 100 , the GTL have enough time to take effect only at $S < 1\%$.

The reason why crystals (and solids in general) are so different from liquids is as follows. Information that a molecule, or an atom, or another growth unit attached to or detached from a liquid droplet surface is spread over the droplet quickly by capillarity surface waves and surface pressure equilibration. On a small crystallite or on a step species sitting in one area of the surface do not “know” what happens on the other until a kink or a step arrive. The latter process is orders of magnitude slower than the waves on liquid surface or pressure equilibration occurring at the speed of sound.

These issues still need further experimental and theoretical analyses.

5. CONCLUSIONS.

The supersaturation taken as the difference, $\Delta\mu/kT$, between actual and equilibrium chemical potentials of crystallizing species entering the growth unit enters the nucleation work. On the other hand, this is the $\exp(\Delta\mu/kT)$ that enters the kink and thus the step rate of growth. Strict order of species in the lattice gives rise to cooperativity within the unit cell. Correlation between the type of species already present in the kink and the one that is supposed to be added induces non-linear dependence of the growth rate on the species activities and geometrical average of the product of the activities entering the growth unit. This non-linearity is supposed to be minimized in stoichiometric solution by adjustment of the ionic activities in the immediate kink and step vicinity.

References to our earlier work on steps with low kink density are made. The capillarity driven shift of equilibrium predicted by the Gibbs-Thomson law over a short step segment with low kink density may have not enough time to be implemented - if other related processes on a surface proceed too fast. For development of a polygonized spiral around screw dislocation, supersaturation as low as $\sim 1\%$ may be considered too high.

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